

## Update on the Aging of PBX 9501 via Free-Radical Oxidation

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**T**he plastic-bonded explosive PBX 9501, used in weapons, is 94.9% by weight HMX explosive, 2.5% nitroplasticizer (NP), 2.5% Estane® 5703, and 0.1% Irganox 1010 stabilizer (anti-oxidant). Estane® 5703, made by Noveon, is a poly(ester urethane) random copolymer (Fig. 1), which serves as a glue that binds the HMX crystals together to allow for machining of high-precision high-explosive parts. The urethane units segregate (phase separate) into “hard” domains that act as physical crosslinks between the “soft” polyester domains. The NP softens the Estane, and together this markedly decreases the mechanical sensitivity of the PBX. However, the Estane slowly degrades in time, and the corresponding effect on the mechanical properties of the PBX raises safety and reliability concerns. Hence, the study of polymer aging is an integral part of the Enhanced Surveillance Campaign.

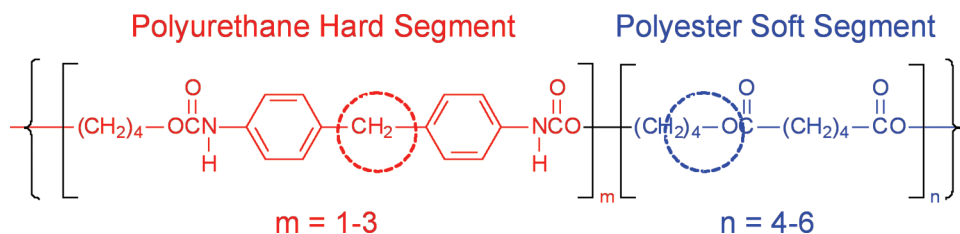
We are studying the chemical mechanisms of degradation processes in PBX 9501 and developing kinetics models. We are working very closely with a large number of experimentalists at the Laboratory and Pantex to determine the chemical and mechanical properties of the PBX and how the two are related. For degradation of PBX in weapons storage, free-radical oxidation of the urethane segments may be as important as the hydrolysis of the polyester segments, especially as the PBX dries out, since the storage environment has both low moisture and oxygen content. Nitroplasticizer (NP) is composed of a mixture of two molecules, bis (2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BDNPF). Various research efforts at the Laboratory

are showing that upon heating NP loses nitro ( $\text{NO}_2$ ) groups and produces oxidizing species that can degrade Estane.

Exciting results on the oxidative degradation of Estane continue to come out of the Constituent Aging Study (CAS, conducted at Pantex). The goals of the CAS are to artificially age the PBX 9501 constituents (HMX, Estane, NP, stabilizer) in 25 different combinations at accelerated rates, detect chemical reactions, identify reaction products and possible degradation mechanisms, and provide data for lifetime prediction modeling. The samples are aged at different temperatures (ranging from 40° to 64° C) in a dry, oxygen-free environment. Over 1000 samples were aged for a period of three years, with typical samples analyzed at half-year intervals. One of the most striking findings is that combinations containing NP (NP + Estane and NP + Estane + stabilizer) show a strong correlation between the total amount of gas products generated and significant changes in the molecular weight (MW) of the Estane.

Based on the rate of evolution of  $\text{NO}_x$  ( $\text{N}_2\text{O}$  and  $\text{NO}$ ) gasses at various temperatures, the Arrhenius parameters (prefactor A and energy of activation  $E_a$ ) for the rate ( $= A \exp(-E_a/RT)$ , R = gas constant) of NP decomposition were determined for eight different CAS constituent combinations. A likely mechanism is that  $\text{NO}_2$  groups dissociate from the NP molecules and subsequently oxidize the carbon atoms in the backbone of the NP molecules as well as oxidize the urethane linkages in Estane. The oxidation of the Estane polymer can cause chain scission (decreased MW) and crosslinking (increased MW and gel formation), while small molecule remnants of the reactions are presumably being detected in the gas analysis. Such large changes in MW can have drastic effects on the mechanical properties of the elastomer. The energy of activation ( $E_a = 28 \text{ kcal/mol}$ ) for the rate of evolution of  $\text{NO}_x$  gasses compares favorably with values determined from an earlier (Wewerka et al., 1976) aging study on PBX 9501.

Fig. 1.  
Chemical structure  
of Estane®.



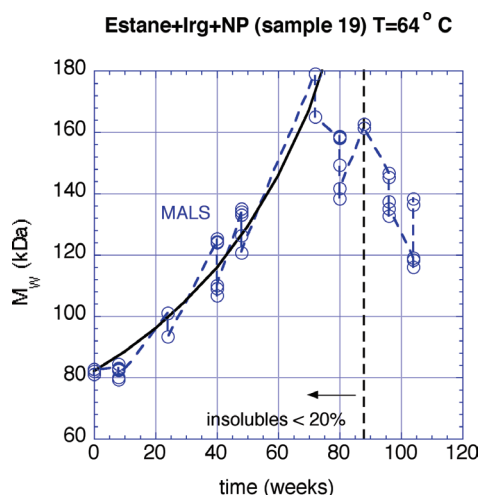
During the course of the CAS, the Estane MW was determined using Gel Permeation Chromatography (GPC) with Light Scattering (MALS) detection. In Fig. 3, the change in Estane MW as a function of time (blue open circles) for sample #19 (Estane + NP + Irganox stabilizer) is presented. The MW increases as a function of time at 64°C indicating that crosslinking is dominating over chain scissioning. The data out to about 70 weeks is well described using the random polymerization theory of Flory and Stockmayer (solid black line) fit with one free parameter (the rate of extent of reaction or crosslinking rate). The data beyond 70 weeks is inaccurate since polymer chains of large MW become insoluble in the GPC solvent (as confirmed with polymer gel recovery measurements). For the three CAS samples analyzed at 64°C, the rate of evolution of NO<sub>x</sub> gasses is about 2–16 times faster than the crosslinking rate.

In another set of experiments (D. Wroblewski and coworkers, in the Los Alamos Materials Science Division, J. M. Lightfoot and coworkers, at Pantex), isotopically labeled model materials were used to understand degradation mechanisms in the binder (Estane + NP) under simulated aging conditions. Isotopic enrichment has been utilized to improve the sensitivity of spectroscopic techniques for observing small quantities of degradation products. Isotopically enriched segmented poly(ester urethane) (PESU) with the nitrogen of the MDI-unit enriched with <sup>15</sup>N were prepared. Samples containing <sup>15</sup>N PESU and NP have been aged at three different temperatures (50, 70, and 85°C). Detection of degradation product(s), one of which is the result of oxidation of the bridging methylene carbon of the MDI unit (blue circle in Fig. 1), was accomplished by 1-D and 2-D NMR techniques. A representative 2-D NMR spectra is shown in Fig. 3. By quantifying the amounts of the oxidized product(s) relative to the starting material at different aging times and temperatures, the kinetics of the degradation process was determined. The rate of oxidation of Estane rate for the degradation of PESU is about the same and two times faster (for 70°C and 85°C, respectively) than the NO<sub>x</sub> gas evolution rate in the decomposition of NP. Furthermore,

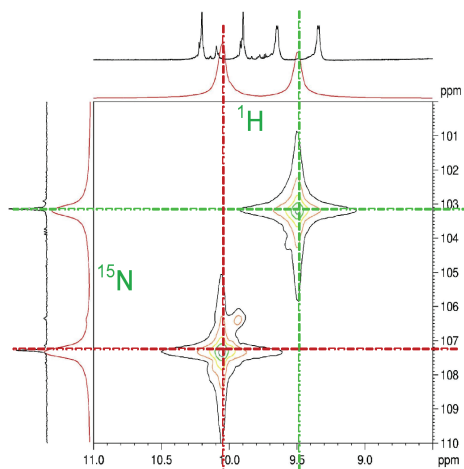
the energy of activation (29 kcal/mol) derived from the NMR study agrees with that (28 kcal/mol) determined from the rate of evolution of NO<sub>x</sub> gasses.

In conclusion, the correlation of the rate of evolution of NO<sub>x</sub> gasses with both: 1) the crosslinking rate from the GPC-MALS MW analysis and 2) the methylene bridge oxidation rate from the NMR analysis suggests a correlation between the decomposition of NP and oxidation of Estane. Future work will include correlating changes in chemical properties of PBX (such as Estane MW) with changes in mechanical properties. (See D. E. Hanson's contribution in this volume on page 93.)

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**Fig. 2.**  
Estane molecular MW as a function of aging time at 64°C.



**Fig. 3.**  
<sup>1</sup>H-<sup>15</sup>N 2-D NMR spectra for PESU/ NP aged at 85°C for 370 days.